Gas Chromatography

Gas Chromatography

1. Uses
   - Separation and analysis of organic compounds.
   - Testing purity of compounds.
   - Determine relative amounts of components in mixture.
   - Compound identification.
   - Isolation of pure compounds (microquantities work).

Gas Chromatography

Similar to column chromatography, but differs in 3 ways:

- Partitioning process carried out between Moving Gas Phase and Stationary Liquid Phase
- Temperature of gas can be controlled
- Concentration of compound in gas phase is a function of the vapor pressure only.

GC also known as:

- Vapor-Phase Chromatography (VPC) and
- Gas-Liquid Partition Chromatography (GLPC)

Gas Chromatograph

- Microliter Syringe.
- Heated injection port with rubber septum for inserting sample.
- Heating chamber with carrier gas injection port.
- Oven containing copper, stainless steel, or glass column.
- Column packed with the Stationary Liquid Phase a non-volatile liquid, wax, or low melting solid-high boiling hydrocarbons, silicone oils, waxes or polymeric esters, ethers, and amides.
- Liquid phase is coated onto a support material, generally crushed firebrick.

Principals of Separation

1. Column is selected, packed with Liquid Phase, and installed.
2. Sample injected with microliter syringe into the injection port where it is vaporized and mixed into the Carrier Gas stream (helium, nitrogen, argon).
3. Sample vapor becomes partitioned between Moving Gas Phase and Stationary Liquid Phase.
4. The time the different compounds in the sample spend in the Vapor Phase is a function of their Vapor Pressure.
5. The more volatile (Low Boiling Point/Higher Vapor Pressure) compounds arrive at the end of the column first and pass into the detector.

Principals of Detection

1. Two Detector Types
   - Thermal Conductivity Detector (TCD).
   - Flame Ionization Detector (FID).
2. TCD is electrically heated “Hot Wire” placed in carrier gas stream
3. Thermal conductivity of carrier gas (helium in our case) is higher than most organic substances.
4. Presence of sample compounds in gas stream reduces thermal conductivity of stream
5. Wire heats up and resistance decreases.
6. Two detectors used: one exposed to sample gas and the other exposed to reference flow of carrier gas.
7. Detectors form arms of Wheatstone Bridge, which becomes unbalanced by sample gas.
8. Unbalanced bridge generates electrical signal, which is amplified and sent to recorder.

Factors Affecting Separation

1. Boiling Points of Components in Sample:
   - Low boiling point compounds have higher vapor pressures.
   - High boiling point compounds have lower vapor pressures requiring more energy to reach equilibrium vapor pressure, i.e., atmospheric pressure.
   - Boiling point increases as molecular weight increases.
2. Flow Rate of Carrier Gas.
3. Choice of Liquid Phase:
   - Molecular weights, functional groups, and polarities of component molecules are factors in selecting liquid phase.
4. Length of Column:
   - Similar compounds require longer columns than dissimilar compounds. Isomeric mixtures often

Uses of GC:

-Introduce the theory and technique of gas chromatography.

-Identify a compound by it retention time.

-From the relationship between peak area and mole content calculate the mole fraction and mole percent of a compound in a mixture.

Approach:

1. Obtain chromatograph of a known equimolar mixture of four standards
2. Obtain chromatograph of unknown mixture (one or more compounds in the known mixture).
3. Determine Retention Times.
4. Calculate Peak Areas
5. Calculate Total Area
6. Calculate Mole Fraction
7. Calculate Mole Percentage.

Gas Chromatography

Results:

-that support the identification of compounds in the "unknown" mixture.

-the known mixture should show:

* definitive peaks that are used for,

* compare the unknown to equivalency of the peak areas in the known mixture and then adjust the peak areas and the computed mole percent of the unknown mixture.

Gas Chromatography instrumentatio

Record Instrument readings

- Injection Port Temp
- Column Temp
- Detector Temp
- Gas Flow Rate (65 mL / min)
- Chart Speed (5 cm / min)

Note: For the older GC's (the two on right), all three temperatures are the same

Injecting the Sample

- Sample is injected into the port with the microsyringe
- The Microsyringe is fragile and expensive – BE CAREFU
- You mark "Starting Point" on chart – short vertical line
- Insert needle fully into rubber septum or until resistanc is met – maybe a ¼ inch remains.
- Inject sample quickly and remove needle.
- Start chart recorder simultaneously with sample injection.

Determination of Retention Time

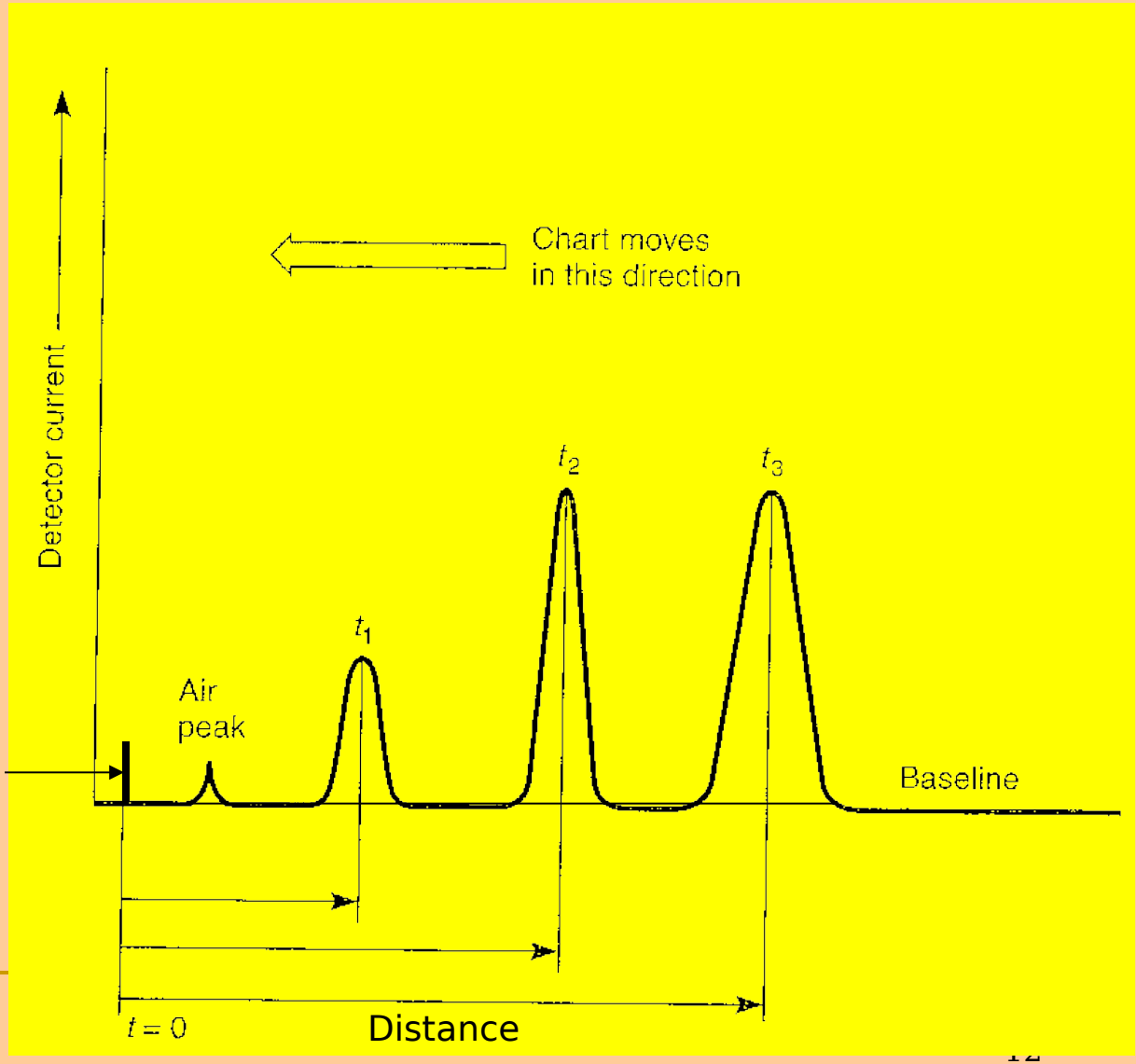
- The period that is required for a compound to pass through the column following injection to the point where the detector current is maximum, i.e. *maximum pen deflection* or *maximum peak height*.
- For a given set of constant conditions (carrier gas, flow rate of carrier gas, column temperature, column length, liquid phase, injection port temperature), **the retention time of any compound is always constant**.
- Retention Time is similar to the "**Retardation Factor, R_f**" in Thin Layer Chromatography.
- Compute Retention Time from the Chart Speed (5 cm/min) and the distance on the chart from the time of injection to the point on the chart where the perpendicular line drawn from the peak height intersects the base line.

Computation of Retention Time

Since: Velocity = Distance / Time

Ret Time = Dist(cm) / Vel(cm/min)

Dist = Distance chart moves in cm
Vel = Velocity of chart in cm/min



Quantitative Analysis

1. The area under a gas chromatograph peak is proportional to the amount (moles) of the compounds eluted.

2. The molar % composition of a mixture can be ≈ comparing the relative areas of the peaks on the chromatogram.

3. This method assumes that the detector is equally sensitive to all compounds and its response is linear.

Triangulation Method of Determining Area Under Peak.

Multiply the height of peak (in mm) above the baseline* by the width of the peak at half the height.

*Baseline is a straight line connecting side arms of peak. *Best if peaks are symmetrical.

Add areas to get total.

Divide each area by total area to get mole fraction

Triangulation Method of Determining Area Under Peak.

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   *Baseline is a straight line connecting side arms of peak .
   **NB: Best if peaks are symmetrical*.

2. Add areas to get total (**TA**).

3. Divide each area by total area to get mole fraction. Peak Area

Peak Area = h x w½ :

whereby h = Peak Height, w½ = width at ½PH value.

(i) Total Peak Area (TA) = A + B
(ii) Mole Fraction (MF) = A/TA, B/TA
(iii) Mole Percent = MF x 100

Gas Chromatography

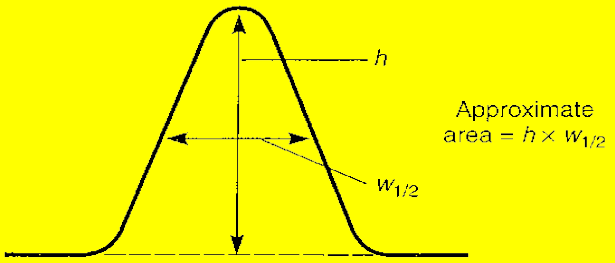

Figure 22.12 Triangulation of a peak.

Area Peak B = 19 x 122 = 2320 mm²
Area Peak A = 17 x 40 = 680 mm²
Total area = 3000 mm²

$\%A = \frac{680}{3000} \times 100 = 22.7\%$
$\%B = \frac{2320}{3000} \times 100 = 77.3\%$
Total 100.0%

} Composition of mixture

Ratio $\frac{B}{A} = \frac{2320}{680} = \frac{3.35}{1}$